# Measurement of the carcinogenic polyaromatic compounds in the exhaust gases of a gasoline internal combustion engine

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## 1 Introduction

In recent years, a considerable effort has been devoted to the solution of one of the most acute environmental problems associated with the pollution of the environment with the substances exhausted by automobile internal combustion engines (ICE). Of these substances, the most hazardous to the health of people are polycyclic aromatic hydrocarbons (PAH). They are not only carcinogenic but also exert pronounced mutagenic and teratogenic effects on the human body. Among the PAH, the most health-hazardous are benzo($\beta$)fluoranthene, benzo(j)fluoranthene, phenanthrene $C_{14}H_{10}$, and especially benz($\alpha$)pyrene $C_{20}H_{12}$, which being a relatively stable chemical compound, can migrate for a long time from one object to another [1]. The indicated compounds are formed in the combustion chambers of engines mainly as a result of the thermal decomposition (pyrolysis) of the heavy fractions of a fuel in the zones with a lack of oxygen, transition from a liquid or gaseous fuel into the combustion products or are synthesized from the more volatile hydrocarbons.

Despite the fact that carcinogenic substances of the PAH category are extremely hazardous to the health of people and to the environment, the works dealing with the formation of these substances and their content in the exhaust gases of automobile engines are very lacking. The existing publications mainly consider the carcinogenic bursts of diesel engines in the limited conditions of their operation [2-4].

At present, the emission of PAH by automobile engines is not normalized. Only carbon monoxide CO and unburnt hydrocarbons $CH_x$, nitric oxide NO, and solid particles are regulated by different international standards (EURO-1 – EURO-6, EPA 10, Post NLT, and others). The content of PAH in the exhaust gases of an ICE depends on many factors: the type of ICE, the mode of its operation, and the composition of the fuel. The present work is devoted to a quantitative analysis of the carcinogenic substances of PAH class in the exhaust gases of an

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automobile gasoline engine operating in two regimes that characterize the extreme conditions of its operation: idle-running ($n = 750 \dots 950\ \text{min}^{-1}$) and under load ($n = 3920 \dots 4320\ \text{min}^{-1}$). These compounds have, as a rule, a negligibly small concentration, and require special methods for their detection. In the present work, we used the gas-chromatography and mass-spectrometry methods for this purpose. These concentrations of 16 compounds of the PAH category in gas samples taken upstream and downstream of an original catalytic neutralizer were determined. Gasolines of octane numbers ON-92, ON-95, and ON-98 were used as a fuel.

## 2 Experimental

The investigations were carried out in an experimental stand designed on the basis of a HONDA D15B2 four-stroke four-cylinder gasoline engine with a distributed fuel injection. Chromatographic analysis was carried out in accordance with the US Compendium Method TO-13A, and its national analog representing the state standard of the Republic of Belarus STB 17.13.05-03-2008/ ISO 11338-1: 2003 “Protection of the Environment and Nature Management. Monitoring of the Environment. Emission of Stationary Sources. Determination of Polycyclic Aromatic Hydrocarbons in Gases and in Particles”: Part 1 “Sampling” and Part 2 “Preparation of Samples, Purification, and Determination”. PAH were separated from exhaust gases with the use of a special system for sampling with a sorbent-containing trap schematically shown in Fig. 1. The sample was then extracted from the sorbent by dichloromethane and analyzed in a gas Agilent Technologies 7890A chromatograph and in Agilent Technologies 5975C mass spectrometer. Figure 2 shows, as an example, the chromatograms for 16 PAH, obtained with the use of the gas-chromatography and mass spectrometry methods for the ICE operating on the ON-92 gasoline in the idle-running regime at $n = 780\ \text{min}^{-1}$. The samples were taken upstream of the exhaust-pipe catalyst.

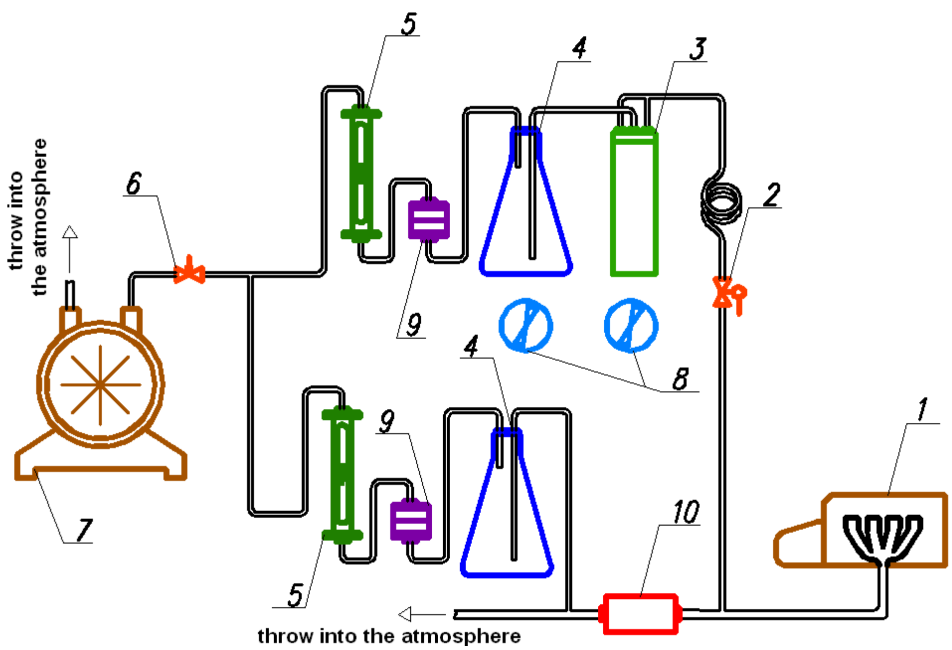

Figure 1. System for taking samples of PAH from the exhaust pipe of an ICE: 1) ICE; 2, 6) cocks-regulators; 3) moisture separator; 4) glass flask; 5) rotameter; 7) facility for drawing off gases; 8) fans; 9) sorbent-containing trap

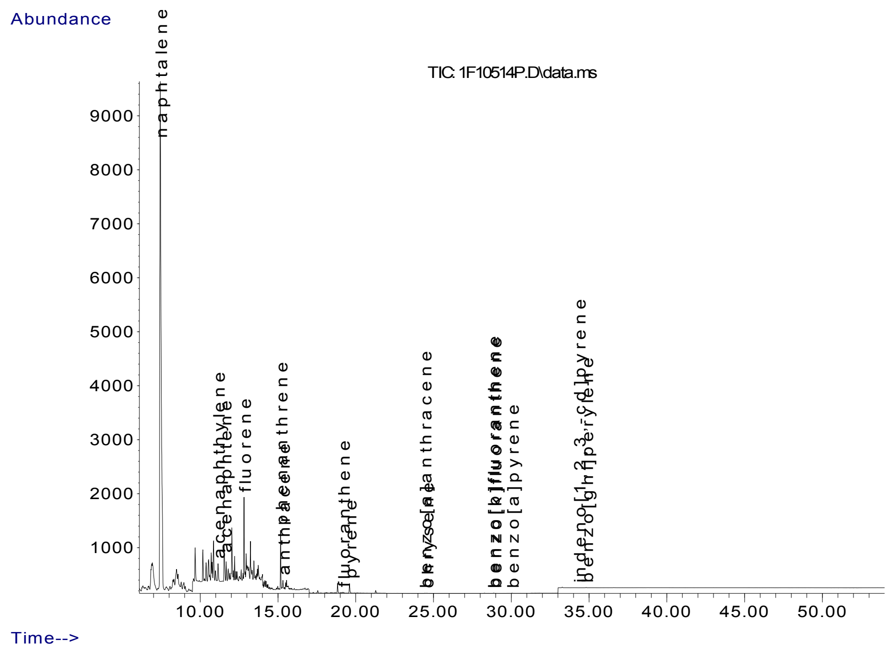


Figure 2. Chromatogram of PAH obtained for the ICE operating in the idle-running regime with an engine speed $n = 780\ \text{min}^{-1}$.

## 3 Measurement results

The concentrations of same PAH in the exhaust gasoline gases in the samples taken downstream of the catalytic neutralizer (practically at the outlet of the exhaust pipe) of the ICE operating in the idle-running regime and in the regime of load are presented in Figs. 3 and 4. In these samples of combustion products, the carcinogenic substances benz(a)pyrene and benz(a)anthracene have been detected, the content of which multiply exceeded the admissible values determined by the World Health Organization (0.12 $\text{ng/m}^3$) and the European Union (1 $\text{ng/m}^3$) for the atmospheric air of inhabited localities [5, 6].

Analysis of the results obtained shows that the concentration of the most toxic substance benz(a)pyrene in the exhaust gases downstream of the catalytic neutralizer of an ICE operating on the ON-92 gasoline in the idle-running regime comprises 0.28 $\mu\text{g/m}^3$, which exceeds the admissible concentration of this substance by hundreds of times. In the case where the ICE operated in the regime of load, the content of benz(a)pyrene in the exhaust gases upstream of the catalytic neutralizer substantially exceeds the admissible values for all of the three gasolines used (24.41, 24.69 and 16.26 $\mu\text{g/m}^3$) for the ON-92, ON-98 and ON-95 gasolines, respectively). The concentration of PAH in the exhaust gases that passed through the catalytic neutralizer of the ICE operating in this regime was decreased as a whole by 20–50 %. For example, the concentration of benz(a)pyrene in the exhaust gases downstream of the catalytic neutralizer was 14.41, 10.47 and 6.25 $\mu g/m^3$ for the ON-92, ON-98 and ON-95 gasolines, respectively (Fig. 4).

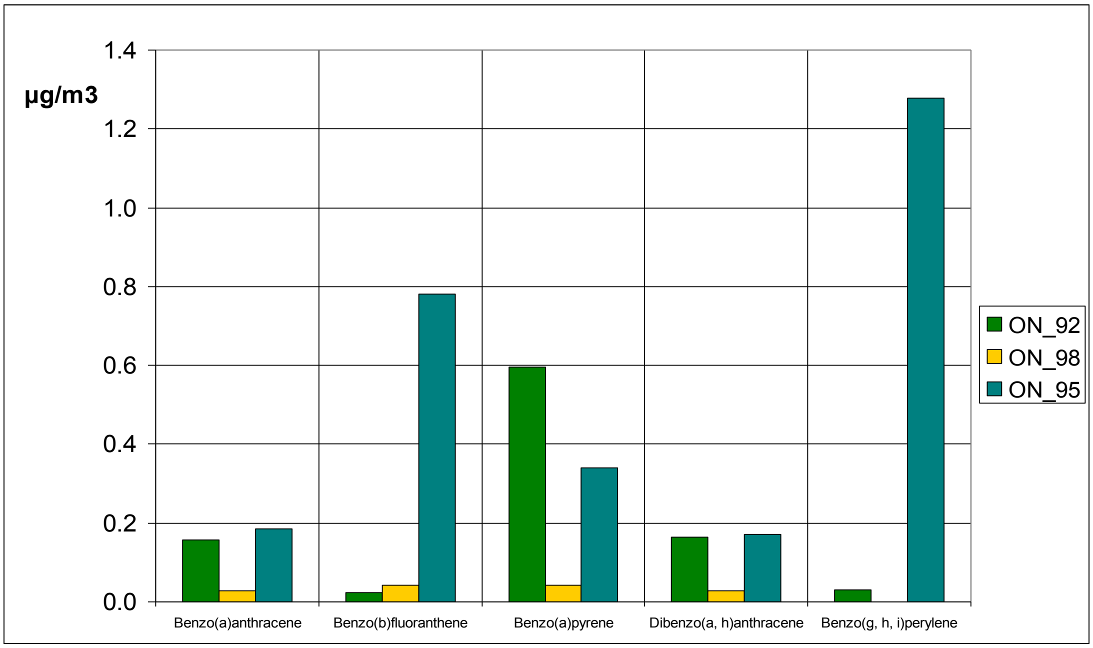


Figure 3. Concentrations of PAH in the exhaust gases downstream of the catalytic neutralizer of the ICE operating in the idle-running regime at $n = 750 \dots 950\ \text{min}^{-1}$.

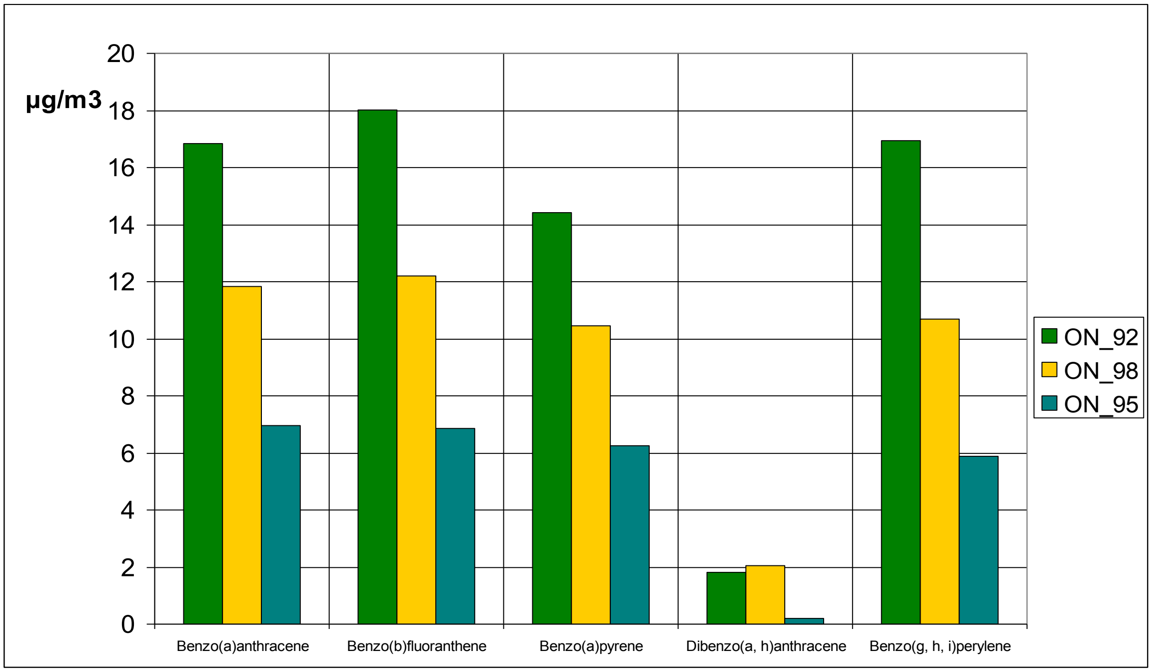


Figure 4. Concentration of PAH in the exhaust gases downstream of the catalytic neutralizer of the ICE operating in the regime of load at $n = 3920 \ldots 4320\ min^{-1}$.

## 4 Conclusions

The emission of carcinogenic substances, in particular of the most hazardous compound benz(a)pyrene, into the atmosphere in the process of operation of an ICE in the characteristic regimes of idle-running and under load multiply exceeds the admissible values recommended by the World Health Organization and the European Union for the air basin of a city. This effect is observed in the combustion products of the ON-92, ON-98, and ON-95 gasolines. It has been established that the amount of each compound in the combustion products of an ICE depends on the regime of its operation and on the gasoline octane number.

## References

[1] Assad M.S., Penyaz'kov O.G. Combustion products of liquid and gaseous fuels: formation, calculating, experiment. Minsk, Belarus Navuka, 2010, 305 p.

[2] Gerald Z. Liu, Devin R. Berg, Victoria N. Vasys, Melissa E. Dettmann, Barbara Zielinska, James J. Schauer. Analysis of $C_1$, $C_2$, and $C_{10}$ through $C_{33}$ particle-phase and semi-volatile organic compound emissions from heavy-duty diesel engines. Atmospheric Environment, 44, 2010. Pp. 1108–1115.

[3] Shu-Mei Chien, Yuh-Jeen Huang, Shunn-Cheng Chuang, Hsi-Hsien Yang. Effects of Biodiesel Blending on Particulate and Polycyclic Aromatic Hydrocarbon Emissions in

Nano/Ultrafine/Fine/Coarse Ranges from Diesel Engine. Aerosol and Air Quality Research, Vol. 9, No. 1, 2009, pp. 18-31.

[4] Shou-Heng Liu, Yuan-Chung Lin, Kuo-Hsiang Hsu. Emissions of Regulated Pollutants and PAHs from Waste-cooking-oil Biodiesel fuelled Heavy-duty Diesel Engine with Catalyzer. Aerosol and Air Quality Research, 12, 2012, pp. 218–227.

[5] WHO guidelines for indoor air quality: selected pollutants. 2010. Pp. 454 (Regional office for Europe. Copenhagen. www.who.euro.int).

[6] Air quality in Europe – 2015 report. European Environment Agency. EEA Report No 5/2015.